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INFLUENCE OF MECHANICAL ACTIVATION ON IMPROVEMENT OF DISPERSION BEHAVIOR OF GOETHITE, QUARTZ AND CLAY MINERALS IN THE PRESENCE OF DIFFERENT DISPERSANTS

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Abstract: The paper focuses on the mechanical treatment of natural goethite,quartz and clay minerals, aiming at improving their dispersion behavior in the presence of different dispersants.
The subject of research of mechanical activation is the change of the state of the material under the action of mechanical forces, whereby the newly created state of the material is defined as "activated". The paper presents tests and analysis of the possibility of applying mechanoactivation of the mineral surface by grinding and multistage grinding in the planetary mill, for improving reactions with surface-active reagents. The results showed that the greatest resistance to grinding has the sample of goethite (Moss hardness 5-5.5). The influence of mechanoactivation was analyzed on the basis of the results of chemical analyzes and the ratio of sediment and overflow masses. Mechanical activation encourages better dispersion when activated minerals are treated with selected dispersants.

Key words: goethite, quartz, clay, mechanical activation, dispersion.

1. INTRODUCTION

The dominant direction in the study of mechanical influences on the composition, structure and properties of materials belonged, until recently, to solid state physics, i.e. elastic-plastic behavior of materials. However, a large number of changes that occur during the action of mechanical energy on the material caused the emergence of a new scientific discipline-mechanochemistry. Mechanochemistry can be defined as a scientific discipline that studies the initiation and acceleration of chemical reactions under the influence of mechanical energy. Regardless of the formulation of mechanochemistry, it is obvious that the subject of its research is the change of the state of the material under the action of mechanical forces, whereby the newly formed state of the material is defined as "activated". The concepts of mechanochemistry and mechanical activation very often overlap. So, the difference between mechanochemistry and mechanical activation is best seen in the fact that mechanical activation is achieved by mechanical action on the material in the absence of another reagent [1-4].

Materials science studies, among other things, the dependence between the composition, structure and properties of materials and their behavior under the influence of thermal, chemical, electromagnetic and mechanical treatment. In the last thirty years, mechanochemistry and mechanical activation has gained more and more importance in the scientific sense. Mechanical activation can be applied in various scientific and technological fields, such as the cement industry, the industry of refractory materials, in the production of fertilizers, drugs and pharmaceuticals, catalysts, mineral processing, and many others. [5-7]. Physico-chemical phenomena that are conditioned by mechanical action on solid bodies are particularly characteristic in the conditions of material grinding. In material operations, especially in fine and ultrafine grinding, mechanical actions take place by compression, shear, and impact-collision. In the most general sense, during mechanical activation, there can be: radiation of electromagnetic waves in a wide range, both light and acoustic, heat production, which can heat the material being ground, stimulation of electron emission, increase of the free surface of the material, elastic and plastic deformations material, deformation of the crystal lattice, breaking of chemical bonds in the material, obtaining very small particles, the dimensions of which are of the same order as the parameters of the crystal lattice.

Mineral processing techniques, such as flotation and flocculation, could be very useful for the recovery of complex ores with large amount of fine particles [8-12]. These techniques often include interfacial processes that depend on mineralogical heterogeneity of fine particles surfaces.

The division of dispersed systems into coarse-dispersed, colloidally-dispersed and molecular-dispersed systems is interesting from the point of view of the tests in this work because the tests refer to sizes from 1 to 25 μm. The separation of useful minerals from mineral sludge can be achieved by introducing selective flocculation thanks to the selective action of chemical compounds - flocculants. Knowing that the prerequisite for successful selective flocculation is a stable dispersed system, in which heterocoagulation should be prevented, it is clear that the pretreatment of minerals using surface-active substances-dispersants is of great importance.

The aim of this study is to define the effect of pretreatment by mechanical activation of natural goethite, clay and quartz minerals on their dispersion and flocculation behavior. These materials are the main components of the sludge which is further generated during the iron ore magnetic concentration in Omarska mine.

2. MATERIALS AND METHODS

2.1. Materials

Natural raw material samples from Omarska mine (Bosnia and Herzegovina), labeled as: “goethite”, “quartz” and “clay” were handpicked. Previously, a detailed characterization of all samples was carried out [13-14]. They have following mineral compositions:

“Goethite” : Goethite (~86%) which dominate over hematite (~10%) and minor contents of quartz (~4%), with chemical composition (in mass %): Fe 57.16, SiO_2 4.44, Al_2O_3 0.59, Mn 1.18 and LOI 10.86; and density of 3,940 (g/cm^3).

“Quartz” : major quartz (~91%) which dominates over clay minerals of illite-sericite - kaolinite composition (~6%) and feldspars (~3%) with chemical composition (in mass %): SiO_2 92.90, Al_2O_3 3.28, Fe 0.74, LOI 1.62; and density of 2.663 (g/cm^3).

“Clay”: major quartz (~50%) and clay minerals (~44%), which dominates over minor goethite (~4%), chloritoid (~2%) and hematite, with chemical composition (in mass %): Fe 3.67, SiO_2 54.45, Al_2O_3 25.20 and LOI 4.80; and density of 2.734 (g/cm^3).

All reagents used were of analytical grade, and they were prepared as solutions in distilled water. The sodium hexametaphosphate (SHMP) and sodium silicate (SS) manufactured by Lach-Ner, s.r.o. (Czech Republic), were used as dispersants. As flocculant, anionic polyacrylamide (PAM) type SUPERFLOC A100, manufactured by Kemira, was used. 5% NaOH was used as pH modifier.

2.2. Methods

All tests of mechanochemical activation of the samples were performed using the laboratory mill “ROCKLAB SRM RING MILL”, MANUAL, where the kinetic energy is transferred directly to the elements that perform the activation of the material particles, in the laboratory Global Research and Development, Mining and Mineral Processing, Maizières-lès-Metz, France. The “MALVERN MASTERSIZER 2000-Dry and Wet” device was used for physical characterization (particle size distribution).

All dispersion and flocculation tests were carried out at a pH value of 10.5 because it was estimated by visual observation that the dispersion exists only at that pH value. All tests were performed in 500 ml beaker, with 12% solid (69 g of solid in 500ml), and 5% NaOH was used to adjust the pH value with pH meter, SENSION™ pH 31, manufacturer HACH Lange GmbH.

The test procedure was:

- mixing time without dispersant (using a magnetic stirrer), 2 min
- mixing time with dispersant (using a magnetic stirrer), 5 min
- deposition time 10 min

• separation of the dressing from the sediment (using a rubber hose for decantation)

• drying in the oven at 105 ˚C and measuring samples (sediment)

• chemicalwet analysis according to BAS ISO 2597-1: 2012 (goethite).

3. RESULTS AND DISCUSSION

3.1. Particle size distribution analyzis

In order to determine the best possible conditions of dispersion, an experiment with sodium hexametaphosphate was performed on each sample. The milling were performed in order to achieve a uniform coarseness of all samples, i.e. a roughness below 25 µm. This implies that 80% of the mass of the sample belongs to the class under 25 µm. In practice, it is usual to achieve the maximum possible uniformity (at least 80% of the mass) by milling. The limonite sludge, already pulverized in the processing process, was not additionally ground and is shown in the graph for comparison.

Particle size distributions of limonite sludge, goethite, clay and quartz are shown on Figures 1, 2 and 3.

The figure 1. shows the results of the particle size distribution analysis of the samples in their natural state, more precisely, as they were taken from the Omarska mine. Limonite sludge was taken from hydrociclon overflow and natural raw material samples (“goethite”, “quartz” and “clay”) were handpicked from the open pit “Buvac” surface mine. Analyzing Figure 1, we can see that 80% of the mass of individual samples belong to different classes, and that all natural samples belong to larger classes than sludge. So, 80% of the mass of the sample of limonite sludge belongs to the class under 15 µm, while 80% of the mass of other samples belongs to the classes below, respectively, goethite 50 µm, quartz 40 µm and clay 30 µm.

These results indicated the need to prolong the grinding of goethite, quartz and clay. Those results are shown in Figure 2. Both quartz and clay were reduced to a size below 25 µm ,but the goethite still remained quite coarse-grained. It is not entirely clear why goethite provides such resistance to grinding because on the Mohs scale goethite have hardness is between 5 and 5.5, while quartz is harder and has a hardness of about 7.

In Figure 3, we observe four sample sieving curves of goethite for comparison. The goethite sample had to be milling twice, because , we did not get a sample of satisfactory particle size. The reason is probably the high resistance to crushing and/or an inadequate milling device (disk mill). After the double milling, it was necessary to sieve the sample on a -53 µm, but even then, we did not get a sample of satisfactory particle size. Therefore, we sieving the sample on two sieves -38 µm and -25 µm. After that, we did achieve a size of 80% -15 µm and sample as prepared for experiment.

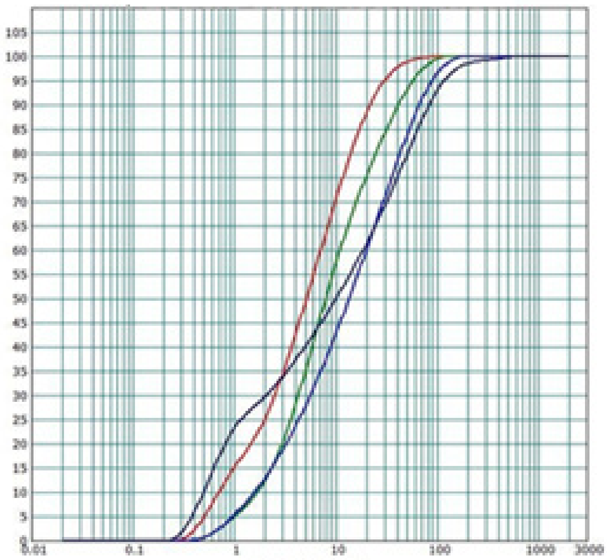

Figure 1. *Particle size distribution of limonite sludge*

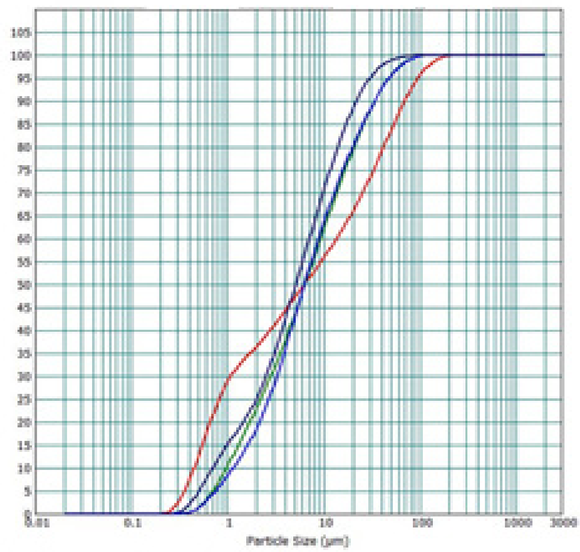

***Figure 2**. Particle size distribution of limonite sludge goethite, quartz and clay before milling goethite, quartz and clay after milling*

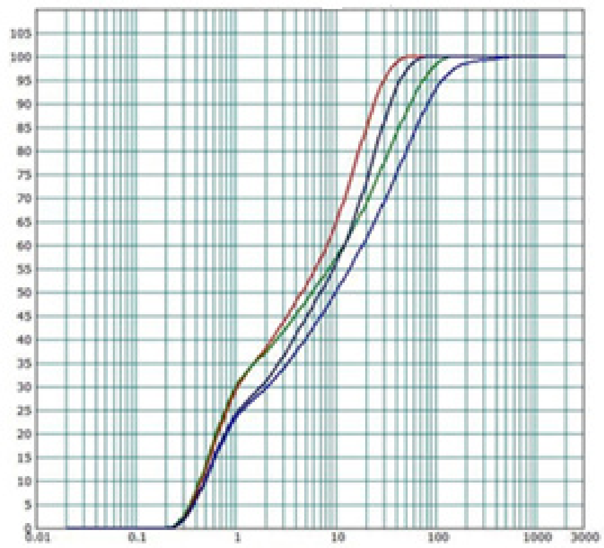

***Figure 3**. Particle size distribution of goethite, after two milling and sieving*

3.2.Influence of the mechanical activation on dispersion behavior

The disperse systems containing natural minerals are always complex due to the heterogeneity of their surfaces. Spontaneous coagulation in such systems occur as a result of different surface charge, more precisely, as a result of the electrostatic attraction of oppositely charged particles. Stable dispersion implies that the repulsive forces between the particles are strong enough to overcome the attractive forces, either electrostatic or Van der Waals forces.This can be achieved by the addition of surface-active substances-dispersants [15].

One of the ways of measuring the effectiveness of dispersants is to measure the mass of dispersed (float) or precipitated (sink) material. The influence of dispersants on the behavior of goethite, quartz and clay before and after grinding and sieving was monitored by measuring the mass of the precipitate, expressed in wt% at different consumptions of dispersants. Inorganic compounds were used as dispersants: sodium silicate (Na_2SiO_3) and sodium hexametaphosphate, ($Na_6P_6O_{18}$). It was expected that the action of dispersants would affect the reduction of the amount of sediment, which was achieved. The additional impact of mechanical activation is visible from Figures 4, 5 and 6. Mechanical activation caused an increase in the active surface, i.e. increased the number of active sites on the surface of the mineral for the action of the dispersant. This is especially pronounced in the case of goethite and quartz. The smaller influence of mechanical activation on the clay sample can be explained by naturally finer clay particles and its complex mineralogical composition.

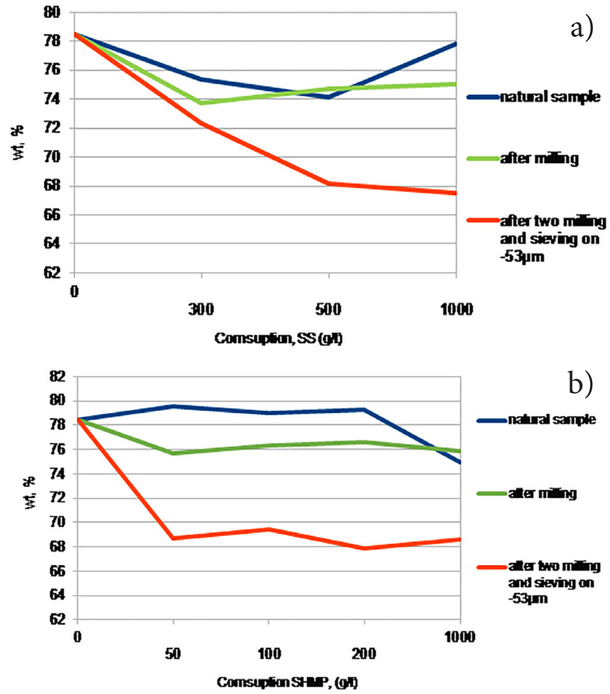

***Figure 4.** Settling of goethite after one and two grindings, in the presence of a) SS, b) SHMP*

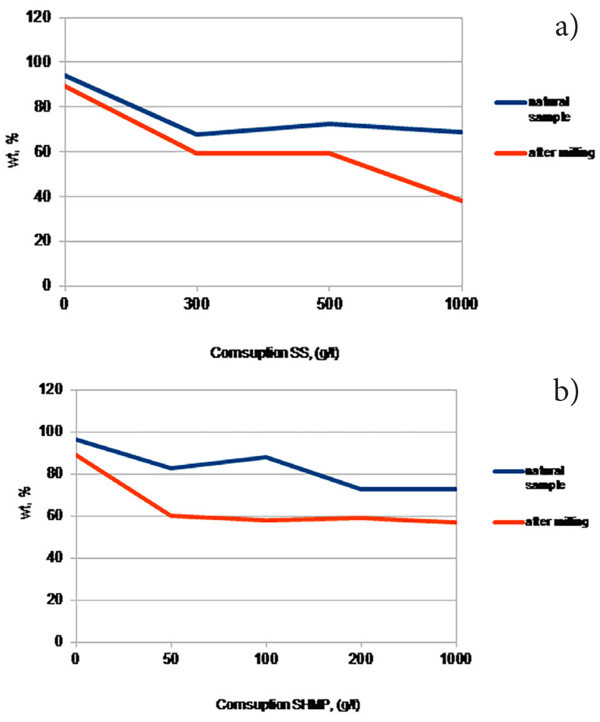

***Figure 5.** Setlling of quartz after grinding, in the presence of a) SS, b) SHMP*

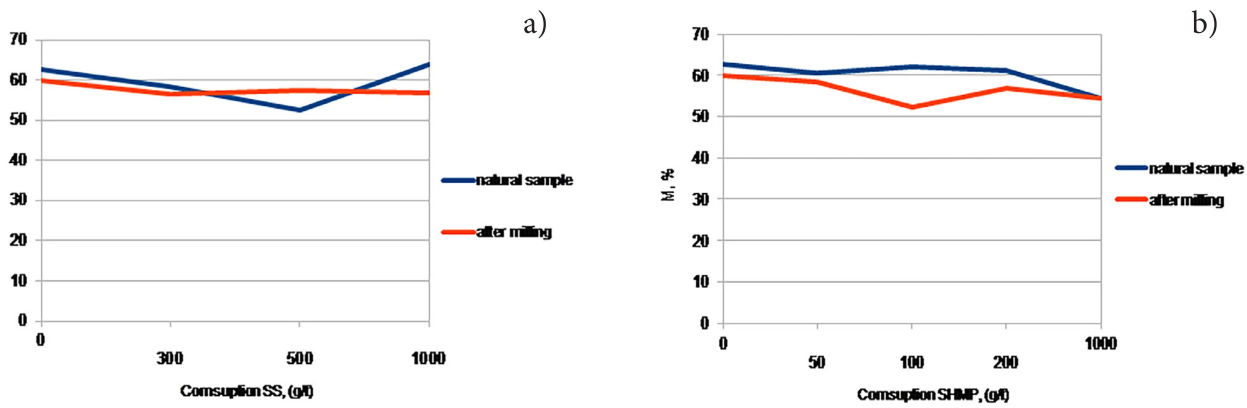

Figure 6. *Setlling of clay with different consumptions after grinding, in the presence of a) SS, b) SHMP*

Figure 7. and 8 show the influence of the concentration /consumption of sodium hexametaphosphate and sodium silicate on the dispersion behaviour of limonite sludge, goethite, quartz and clay samples. It can be seen that dispersant consumption does not play a role in dispersion stability, which is favorable from an environmental point of view. In addition, the performance is better in the case of hexametaphosphate, so it was chosen as a dispersant in further research.

Considering that mechanical activation, as mentioned earlier, can also cause other changes, e.g. breaking chemical bonds, increasing solubility, etc., analysis of chemical composition of goethite sample was also carried out. The results are presented in Table 1. It is clearly seen that there are no differences in the chemical composition neither in the dispersion nor in the precipitated phase.

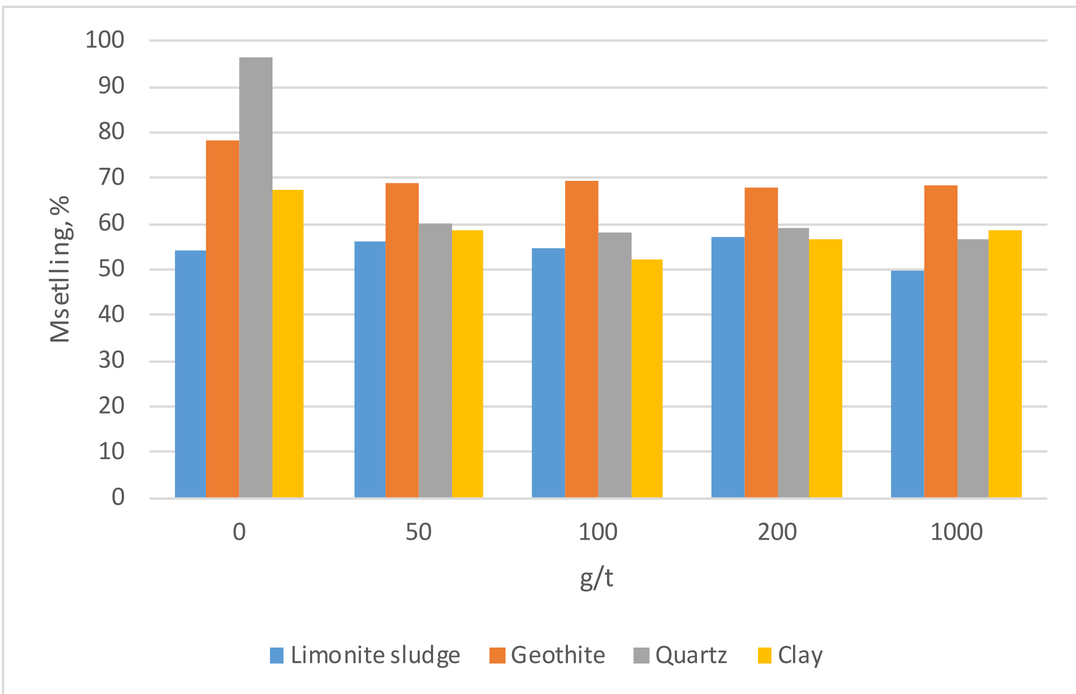

Figure 7. *Setlling of limonite sludge, goethite, quartz and clay depending on consumptions of SHMP after milling*

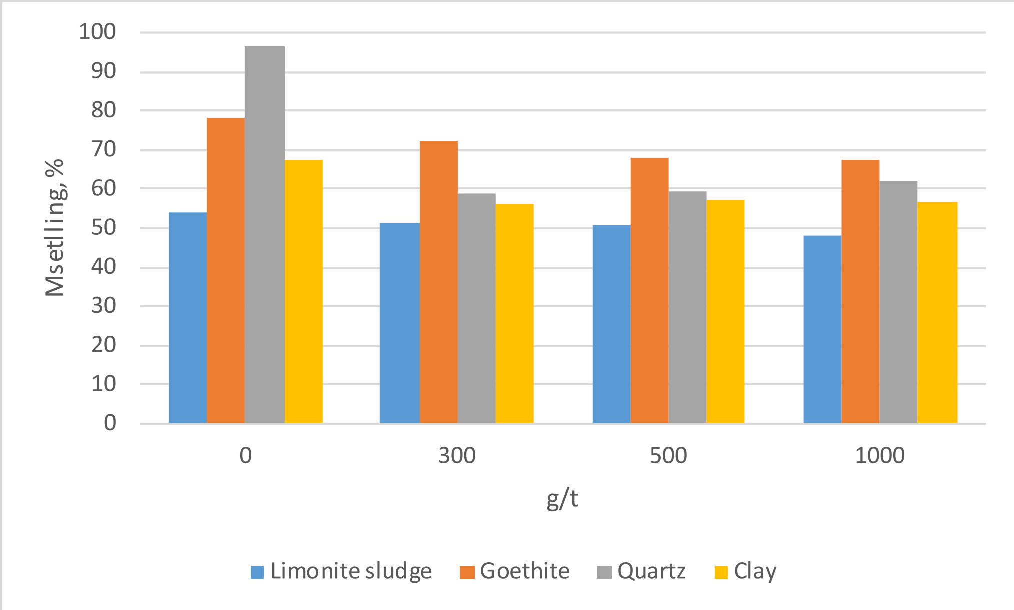

Figure 8. *Setlling of limonite sludge, goethite, quartz and clay depending on consumptions of SS after milling*

Table 1. *The chemical composition of goethite in the dispersed (float) and precipitated (sink) phase after mechanical activation*

Reagents	Consumption, g/t	After 1 x milling							After 2 x milling and sieving -53µm						
		Product	Mass %	Fe, %	SiO_2, %	Al_2O_3, %	Mn %	LOI,%	Product	Mass, %	Fe, %	SiO_2, %	Al_2O_3, %	Mn, %	LOI,%
SHMP	50	Float	20.4	57.4	2.9	0.8	1.6	10.8	Float	31.3	57.1	3.0	0.7	1.5	10.8
		Sink	79.6	57.4	4.9	0.5	1.1	11.0	Sink	68.7	56.6	5.2	0.6	1.2	11.0
	100	Float	21	57.7	2.9	0.8	1.6	10.7	Float	30.6	57.4	3.0	0.7	1.5	10.8
		Sink	79	57.2	4.9	0.5	1.1	10.5	Sink	69.4	56.6	5.2	0.6	1.2	10.9
	200	Float	20.7	57.6	2.9	0.8	1.6	10.7	Float	32.1	57.4	3.1	0.7	1.5	10.7
		Sink	79.3	56.8	4.9	0.5	1.1	11.0	Sink	67.9	56.1	5.2	0.6	1.2	10.9
	1000	Float	24.1	n.a.*	n.a.*	n.a.*	n.a.*	n.a.*	Float	31.4	57.3	3.0	0.7	1.5	10.7
		Sink	75.9	n.a.*	n.a.*	n.a.*	n.a.*	n.a.*	Sink	68.6	56.1	5.2	0.6	1.2	11.0
SS	300	Float	24.6	56.6	3.5	0.9	1.6	10.6	Float	27.7	57.2	3.4	0.8	1.5	10.9
		Sink	75.4	56.7	5.1	0.5	1.1	10.9	Sink	72.3	56.6	5.1	0.6	1.2	10.9
	500	Float	25.8	57.2	3.2	0.8	1.6	10.7	Float	31.9	57.6	3.2	0.7	1.5	11.0
		Sink	74.2	56.3	5.4	0.5	1.1	10.9	Sink	68.1	56.4	5.3	0.6	1.2	10.9
	1000	Float	22.2	56.7	3.4	0.9	1.6	10.6	Float	32.5	56.7	3.3	0.7	1.5	10.9
		Sink	77.8	56.2	5.0	0.5	1.1	10.9	Sink	67.5	56.3	5.3	0.6	1.2	10.8
Without reagents		Float	21.5	57.1	3.0	0.8	1.6	10.6							
		Sink	78.5	56.5	5.0	0.5	1.1	11.0							
		Total	100	57.2	4.4	0.6	1.2	10.9							

n.a.* not analyzed

4. CONCLUSION

The paper examines the influence of mechanical activation on improving the dispersibility properties of the natural minerals goethite, quartz and clay from the Omarska iron ore mine. Two inorganic compounds were used as dispersants: sodium silicate (Na_2SiO_3) and sodium hexametaphosphate, ($Na_6P_6O_{18}$).

Mechanical activation affects the increase of mineral surface activity, but does not affect the chemical composition. One can noticed that with mechanical activation there is an increase in the active surface of the mineral samples for the action of dispersants. This results in a more stable dispersion and an increase in the proportion of fine particles in the floating part. This is especially pronounced in the case of goethite and quartz.

The analysis of the particle size distribution showed that the samples of goethite, quartz and clay had to submitted to be further grinding in order to achieve the required coarseness. Also, goethite showed the greatest resistance to grinding. For this reason, the goethite had to be ground twice and sieved to achieve the desired coarseness class. Longer grinding increases the number of active sites on the surface of the mineral and thereby achieves a better effect of dispersants.

The dispersant consumption does not play a role in dispersion stability. Sodium hexametaphosphate, ($Na_6P_6O_{18}$) showed better results in all investigated cases than sodium silicate (Na_2SiO_3).

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УТИЦАЈ МЕХАНОАКТИВАЦИЈЕ НА ПОБОЉШАЊЕ ДИСПЕРЗИЈЕ ГЕТИТА, КВАРЦА И ГЛИНЕ У ПРИСУСТВУ РАЗЛИЧИТИХ ДИСПЕРЗАНАТА

Сажетак: Рад се бави механичким третманом природног гетита, кварца и минерала глине. са циљем побољшања њиховог дисперзионог понашања у присуству различитих дисперзаната. Предмет истраживања механичке активације је промјена стања материјала под дејством механичких сила, при чему се новонастало стање материјала дефинише као „активирано". У раду су приказана испитивања и анализа могућности примјене механоактивације минералне површине мљевењем и вишестепеним мљевењем у планетарном млину, за побољшање реакција са површински активним реагенсима. Резултати су показали да највећу отпорност на мљевење има узорак гетита (тврдоћа по Moss-u 5-5,5). Утицај механоактивације је анализиран на основу резултата хемијских анализа и односа масе седимента и преливне масе. Механичка активација подстиче бољу дисперзију када се активирани минерали третирају одабраним дисперзантима.

Кључне ријечи: гетит, кварц, глина, механичка активација, дисперзија.

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